

CHAPTER 2

EPA/NSF ETV EQUIPMENT VERIFICATION TESTING PLAN FOR REMOVAL OF ARSENIC BY ION EXCHANGE

Prepared by:
NSF International
789 Dixboro Road
Ann Arbor, MI 48105

Copyright 2000 NSF International 40CFR35.6450.

Permission is hereby granted to reproduce all or part of this work, subject to the limitation that users may not sell all or any part of the work and may not create any derivative work therefrom. Contact Drinking Water Systems ETV Pilot Manager at (800) NSF-MARK with any questions regarding authorized or unauthorized uses of this work.

TABLE OF CONTENTS

1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN	2-5
2.0 INTRODUCTION.....	2-5
2.1 Arsenic Speciation and Occurrence.....	2-5
2.2 The Arsenic Ion-Exchange Process.....	2-6
2.2.1 Effect of Sulfate on Arsenic Removal.....	2-7
2.2.2 Effect of Multiple Contaminants.....	2-7
2.2.3 Low Effluent pH in the Early Stages of Exhaustion.....	2-8
2.2.4 Spent Brine Reuse and Treatment	2-8
3.0 GENERAL APPROACH.....	2-9
4.0 OVERVIEW OF TASKS.....	2-9
4.1 Task 1: Selection and Characterization of Feed Water	2-9
4.2 Task 2: Preparation, Coordination and Startup	2-9
4.3 Task 3: Initial Plant Characterization	2-10
4.4 Task 4: Verification Testing Runs.....	2-10
4.5 Task 5: Data Management.....	2-10
4.6 Task 6: Quality Assurance and Quality Control, QA/QC.....	2-10
5.0 TESTING PERIODS	2-11
6.0 DEFINITIONS	2-11
7.0 TASK 1: SELECTION AND CHARACTERIZATION OF FEED WATER.....	2-17
7.1 Introduction	2-17
7.2 Objectives	2-18
7.3 Work Plan.....	2-18
7.4 Schedule.....	2-20
7.5 Evaluation Criteria	2-20
8.0 TASK 2: PREPARATION, COORDINATION, AND STARTUP	2-21
8.1 Introduction	2-21
8.2 Objective.....	2-21
8.3 Work Plan.....	2-21
8.4 Schedule.....	2-22

TABLE OF CONTENTS (continued)

9.0 TASK 3: INITIAL PLANT CHARACTERIZATION.....	2-22
9.1 Introduction	2-22
9.2 Objective.....	2-22
9.3 Work Plan.....	2-23
9.3.1 Arsenic Spiking.....	2-23
9.3.2 Attainment of Steady State Operation	2-24
9.3.3 Collection of Preliminary Data	2-24
9.3.4 Determination of Variable Effluent Quality and Arsenic Peaking Potential.....	2-25
9.3.5 Preliminary Assessment of Plant Performance:	2-26
9.4 Schedule.....	2-26
 10.0 TASK 4: VERIFICATION TESTING RUNS.....	 2-26
10.1 Introduction	2-26
10.2 Objectives	2-26
10.3 Work Plan	2-27
10.3.1 Plant Operating Conditions and Equipment Performance.....	2-27
10.3.2 Feed Water and Product Water Quality	2-27
10.3.3 Arsenic Removal Performance	2-30
10.4 Schedule.....	2-31
10.5 Evaluation Criteria.....	2-31
10.5.1 Treatment Equipment Performance.	2-31
10.5.2 Product Water Quality	2-32
10.5.3 Arsenic Removal Performance	2-32
 11.0 TASK 5: DATA MANAGEMENT.....	 2-32
11.1 Introduction	2-32
11.2 Objectives	2-33
11.3 Work Plan	2-33
11.3.1 Data Handling.....	2-33
11.3.2 Statistical Analysis	2-34
 12.0 TASK 6: QUALITY ASSURANCE/QUALITY CONTROL.....	 2-35
12.1 Introduction	2-35
12.2 Objectives	2-35
12.3 Work Plan	2-35
12.3.1 Daily QA/QC Verifications	2-35
12.3.2 Bi-weekly QA/QC Verifications.....	2-36
12.3.3 QA/QC Verifications for Each Test Period.....	2-36
12.4 On-Site Analytical Methods.....	2-36

TABLE OF CONTENTS (continued)

12.4.1 pH	2-36
12.4.2 Sulfate, Nitrate, Chloride and Alkalinity by Test Kits.....	2-36
12.4.3 Conductivity	2-37
12.4.4 Temperature (Optional for Ion Exchange).....	2-37
12.4.5 Color	2-37
12.5 Chemical and Biological Samples Shipped Off-Site for Analyses	2-37
13.0 OPERATIONS & MAINTENANCE (O&M)	2-38
13.1 Maintenance	2-38
13.2 Operation	2-39
13.2.1 Operation Manuals:.....	2-39
13.2.2 Troubleshooting Guide:	2-40
13.2.3 History of Ion Exchange Package Plant Operability:.....	2-40
14.0 REFERENCES.....	2-41

TABLES

Table 1	Generic Schedule for Verification Testing Plan Completion.....	2-11
Table 2	Historical Water Quality Data	2-19
Table 3	Operation and Performance Data from Verification Test Runs.....	2-28
Table 4	Water Quality Sampling and Measurement Schedule	2-29
Table 5	Analytical Methods	2-30

1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN

This document is the NSF Equipment Verification Testing Plan for evaluation of water treatment equipment for arsenic removal utilizing the ion exchange process. This Testing Plan is to be used as a guide in the development of Field Operations Document (FOD) procedures for testing ion exchange equipment, within the structure provided by the NSF Protocol Document entitled "Protocol for Equipment Verification Testing for Arsenic Removal." This Equipment Verification Testing Plan is applicable only to ion-exchange processes that use strong-base anion resin beads in fixed or moving packed beds.

In order to participate in the equipment verification process for ion exchange, the equipment Manufacturer shall employ the procedures and methods described in this test plan and in the referenced NSF Protocol Document as guidelines for the development of the Field Operations Document. The procedures shall generally follow those Tasks related to Verification Testing that are outlined in this test plan, with changes and modification made for adaptations to specific equipment. Each Field Operations Document shall include Tasks 1 through 6 as defined below. And, at a minimum, the format of the procedures written for each Task should consist of the following sections:

- (1) Introduction,
- (2) Objectives,
- (3) Work Plan,
- (4) Analytical Schedule,
- (5) Evaluation Criteria.

2.0 INTRODUCTION

2.1 Arsenic Speciation and Occurrence

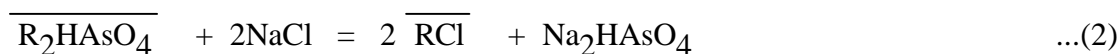
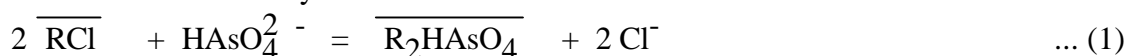
Arsenic has been found in many of the nations drinking water supplies, and, at these trace levels, chronic exposure can cause liver, lung, kidney, and bladder cancer in addition to the previously determined risk of skin cancer (Smith, 1992). Of the chemical constituents that present the greatest health threat in public ground water supplies in the USA, arsenic was accorded the highest priority. Arsenic toxicity depends on its chemical form, with inorganic forms of arsenic more toxic than the organic forms. Inorganic arsenic can be present as the anionic and neutral forms arsenate, As(V), and arsenite As(III). Although As (III) is acutely more toxic, human metabolic processes can convert As (V) to As (III). Thus, current and proposed Environmental Protection Agency (EPA) regulations on arsenic in drinking water deal only with total arsenic, which includes As(III), As(V) and organic arsenic. Because of its lower toxicity and the fact that (a) it is rarely found in ground water, and (b) its concentration in surface water rarely exceeds 5 µg/L, organic arsenic is not dealt with in this Verification Testing Plan. With regard to inorganic arsenic, either As(V) or As(III) or a mixture of the two may be found in arsenic-contaminated ground water. Surface waters contaminated with inorganic arsenic are expected to contain predominantly As(V) because they are in contact with the atmosphere. The ion exchange process

is designed to remove only As(V), thus, if As(III) is to be removed, it must be oxidized, e.g., by chlorine, to As(V) prior to treatment (Frank and Clifford, 1986).

2.2 The Arsenic Ion-Exchange Process

Typically, oxidized and filtered raw water is passed through a bed of chloride-form strong-base anion (SBA) resin (RCl), and the chloride-arsenate ion-exchange reaction, Eq. (1), takes place to yield resin in the arsenate form ($\overline{\text{R}_2\text{HAsO}_4}$). When the column capacity for arsenic is

exhausted, the arsenic “breaks through” into the effluent, and its concentration rises rapidly and generally exceeds the influent arsenic concentration if run beyond breakthrough. The reaction is easily reversed, and regeneration, according to Eq. (2), returns the resin to the chloride form, ready for another exhaustion cycle:



Although chloride-arsenate ion exchange appears simple, several issues must be addressed when implementing the process for drinking water treatment. Among the important factors that would be expected to influence Verification Testing are the following: (1) effect of competing ions such as sulfate, (2) multiple contaminants such as arsenic and nitrate, (3) low pH of the column effluent early in the run, and (4) spent brine reuse and treatment. If the source water has < 500 mg/L TDS and < 220 mg/L sulfate, ion exchange may be the arsenic-removal process of choice. As mentioned, preoxidation to convert As(III) to As(V) is necessary (Frank and Clifford, 1986), but pH adjustment is not because the chloride-arsenate exchange reaction takes place readily in the pH range of natural waters.

The main advantages of the ion-exchange process for removing arsenic from water are as follows:

- (1) The process is simple, robust, compact, easy to automate, and can be operated on-demand.
- (2) It is routinely possible to lower arsenic to less than 1 µg/L.
- (3) Water recovery rates ≥95% are possible.
- (4) No feed water pH adjustment is necessary; the process works very well in the usual pH range of natural waters (6.5-9.2).
- (5) The potential problems with variable effluent water quality including low pH and potential nitrate and arsenic peaking can be solved by operating several columns in parallel and at different stages of exhaustion.
- (6) Exhausted resin can be easily regenerated using salt (NaCl) solution, and the spent regenerant can be reused directly without treatment to remove arsenic.

Potential problems with the ion exchange process for arsenic removal are of the are as follows:

- (1) As(III) when present must be converted to As(V) for efficient removal.
- (2) High sulfate and TDS can reduce run length significantly.
- (3) Because sulfate is more preferred than As(V) and nitrate, arsenic and nitrate peaking can occur if their breakthroughs are exceeded.
- (4) Effluent pH can be reduced to as low as 5.0 in the first 100 BV due to bicarbonate conversion to carbonate and CO₂ by the resin.
- (5) Prefiltration, upstream of the ion-exchange column, may be required to prevent resin fouling.
- (6) Spent brines require disposal.

2.2.1 Effect of Sulfate on Arsenic Removal

Because arsenic is a trace species, its concentration does not greatly influence the run length to arsenic breakthrough. However, because sulfate, a common ion, is preferred over arsenate, nitrate, chloride, bicarbonate, and most other common anions, its concentration largely determines the run length to arsenic breakthrough. For example in a low-sulfate (5 mg/L) water in McFarland, California, arsenic run length exceeded 3500 bed volumes (one bed volume is a quantity of treated water equal to the volume of the resin bed). On the other hand, a McFarland, California water spiked to contain 220 mg/L sulfate, the arsenic run length was only 250 BV. Thus, in testing an ion exchange process for arsenic removal, considerable attention must be paid to the background sulfate concentration.

Not only does increasing sulfate concentration lead to shorter arsenic-removal runs, it leads to chromatographic peaking of arsenic or “dumping” after arsenic breakthrough. For example, arsenic effluent concentration peaks in the range of 1.3 to 6 times the raw water arsenic concentration would not be unusual following arsenic breakthrough. Of course, these peaks would normally be avoided by stopping a run at or before arsenic breakthrough. Another way of coping with the potential peaking of arsenic or any other contaminant less preferred than sulfate is to exhaust several columns in parallel and in different stages of exhaustion. Thus, if one column does run beyond breakthrough, its effluent arsenic peak is diluted by the arsenic-free effluents from the other columns. The columns operated in parallel may be fixed or in motion as is the case with the carousel moving bed designs.

2.2.2 Effect of Multiple Contaminants

Often, sub-MCL levels (< 10 mg NO₃-N/L) of nitrate will be present along with arsenic as a drinking water contaminant, and, for a time, the ion exchange system will remove both nitrate and arsenic. However, nitrate will generally break through before arsenic and sulfate, and a nitrate peak will appear in the effluent if the column if it is allowed to run to

arsenic breakthrough. To avoid the nitrate peak in the event it would exceed the nitrate MCL, the column may be stopped at nitrate rather than arsenic breakthrough. This will lead to shorter run lengths, but will avoid exceeding the nitrate MCL even for a short time. Another approach to avoiding the nitrate peak is to exhaust multiple, fixed or moving, beds in parallel. Even if one of the beds is subject to a nitrate peak, effluents from the other beds will dilute and smooth out the peak.

The implication of multiple contaminants on the Verification Testing Plan is that the Field Operations Document must address the potential problem of multiple contaminants and explain how the testing plan will deal with the issue if it is present.

2.2.3 Low Effluent pH in the Early Stages of Exhaustion

When a chloride-form strong-base anion exchange resin is used to treat natural water as in the arsenic ion exchange process, the effluent pH during the first 50-300 bed volumes can be significantly reduced compared with the influent pH. For example, effluent pHs as low as 5.0 can be observed (Clifford, 1990; Benjamin, 1998). The reason for the pH reduction is the conversion of bicarbonate to carbonate within the resin (Horng and Clifford, 1997). This conversion occurs with the resulting expulsion of a proton (H^+ ion), which increases the H^+ ion concentration and lowers the pH. The bicarbonate-to-carbonate reaction occurs because all standard SBA resins prefer divalent, e.g., carbonate, to monovalent, e.g., bicarbonate, ions at the typical TDS levels found in drinking water supplies. (An exception to this preference for divalent ions occurs with the so-called nitrate-selective, or nitrate over sulfate selective (NSS) resins, which are designed to prefer monovalent nitrate to divalent sulfate. The NSS resins do not exhibit the pH lowering effect.)

The extent of the pH lowering depends primarily on the characteristics of the resin and the bicarbonate concentration in the raw water. Because seriously acidic pHs must be avoided when delivering treated water into a distribution system, the pH of the ion-exchange system under Verification Testing for arsenic removal must be measured and recorded.

As is the case with potential arsenic and nitrate peaking, it is possible to avoid the low pHs observed during the early stages of a single column anion exchanger run by exhausting multiple columns in parallel. In this way the low-pH column effluent from one of the columns will be blended with the other column effluents to produce a neutral-pH water. Again, the parallel columns may be fixed or moving beds.

2.2.4 Spent Brine Reuse and Treatment

It has been found that direct reuse of the spent arsenic-contaminated ion-exchange brine is possible for regeneration of the spent resin (Clifford and Ghurye, 1998). Brine reuse can substantially cut down on (a) the volume of brine discharged and (b) the salt (NaCl) consumption by the process.

With or without brine reuse, the Field Operations Document must address the issue of volume and mass of brine discharge from the plant under test. If the once-used or recycled brine is decontaminated by iron or alum precipitation to remove arsenic before discharge, the volume and solids concentration of the sludge must also be determined along with the arsenic concentration of the dried sludge and the TCLP test result for the sludge.

3.0 GENERAL APPROACH

Testing of equipment covered by this Verification Testing Plan will be conducted by an NSF-qualified Field Testing Organization (FTO) that is selected by the Manufacturer. Water quality analytical work to be carried out as a part of this Verification Testing Plan will be contracted with a state-certified or third-party or EPA-accredited analytical laboratory.

4.0 OVERVIEW OF TASKS

The following section provides a brief overview of the recommended tasks that may be included in Initial Plant Characterization Tests and of the tasks required to be included in the arsenic ion exchange Verification Testing program.

4.1 Task 1: Selection and Characterization of Feed Water

Generally, the ion exchange plant to be tested will be installed and started up at the selected location just prior to implementing the Verification Testing Plan. The test location should be chosen so as to be representative of a class of arsenic contaminated drinking waters to which the particular ion exchange process would be applied. For example, if the primary intended use of the plant is arsenic contaminated ground water, then it should be tested on ground water rather than surface water or arsenic-spiked surface water. Similarly, if the intended use is primarily surface water, it should be tested on surface water because ground waters will be lower in particulates and total organic carbon (TOC).

The objective of Task 1 is to obtain a chemical and physical characterization of the feed water. Generally a ground water with representative arsenic, sulfate, nitrate and TDS concentrations will be selected for Verification Testing. The depth of the well and historical data on water quality parameters should be recorded. However, if a surface water is chosen, a brief description of the watershed that provides the feed water shall be provided, to aid in interpretation of feed water characterization.

4.2 Task 2: Preparation, Coordination and Startup

Orientation meetings will be held, preferably at the plant site. The manufacturer will meet with the testing organization personnel to explain the process, the detailed plant design, the testing program and the schedule. Discussion of the program, its objectives, and responsibilities of each

participant will be clarified. If the plant is not already operating, it is recommended that the manufacturer start it up with representatives of the testing organization present for training purposes.

4.3 Task 3: Initial Plant Characterization

The manufacturer may choose to make predictions of the plant's performance based knowledge of the ion exchange process and the water quality characterization. Preliminary tests will be conducted to measure the plant's basic performance including, for example, the arsenic leakage and run length to arsenic breakthrough. These tests will produce baseline information, which can be used to evaluate changes that occur as the plant ages. If the plant does not meet water quality objectives, the manufacturer will be notified and adjustments made. Alternatively, further testing may be canceled at this point.

4.4 Task 4: Verification Testing Runs

This task, which comprises the actual Verification Testing Runs, is the core of the Verification Testing Plan. During this task, the arsenic-removal ion exchange plant shall be operated for at least 240 hours over a period of at least 14 days during one testing period to collect data on equipment performance and water quality for purposes of performance verification. If a manufacturer chooses to demonstrate the effectiveness of their plant under a significantly different set of background water conditions, the option exists for a second test period to be carried out at a different site with the same transportable ion-exchange plant.

The objectives of the Verification Testing Runs are to (a) observe and record the plant operating conditions and equipment performance, (b) determine the overall feed water and finished water quality, and (c) establish the arsenic-removal performance of the plant.

4.5 Task 5: Data Management

The objective of this task is to establish an effective field protocol for data management at the field operations site and for data transmission between the Field Testing Organization and the NSF for data obtained during Verification Testing, plus the requirement for statistical analysis of the data.

4.6 Task 6: Quality Assurance and Quality Control

An important aspect of Verification Testing is the protocol developed for quality assurance and quality control. The objective of this task is to assure accurate measurement of operational and water quality parameters during Verification Testing of the arsenic ion exchange plant.

5.0 TESTING PERIODS

The required tasks in the Verification Testing Plan (Task 4) are designed to be carried out over one 240-hour period, not including the time required for mobilization, start-up, and Initial Operations. See Table 1 for additional details of the schedule, which includes time for planning, coordination, startup, and initial plant characterization.

Table 1. Generic Schedule for Verification Testing Plan Completion			
Test period	Planning, Coordination and Startup, Estimated Time ^{&}	Initial Plant Characterization, Estimated Time [†]	Verification Testing Runs, Estimated Time ^{**}
1	1-2 weeks	4-6 weeks	240 hrs over 14 days
<p>* Only one test period will be required if the water quality at the site is constant as is the case with many ground waters. If a manufacturer chooses to demonstrate the effectiveness of their plant under a significantly different set of background water conditions, the option exists for a second test period to be carried out at a different site with the same transportable ion-exchange plant.</p> <p>& Time for planning, coordination, and startup will depend on whether the plant is already in operation and level of familiarity of Field Test Organization with details of plant operation and Field Operations Document.</p> <p>† Initial Plant Characterization time may be shortened considerably if the plant is already in operation. If a second test is conducted at a different site, the Initial Plant Characterization tests may take as long as at the first site.</p> <p>**Verification Testing Runs may take as little as 240 hours total elapsed time during a period of 14 days of non-continuous operation. Plant operation, especially with regard to starting and stopping, should be similar to what is expected during normal operation at an actual installation.</p>			

6.0 DEFINITIONS

Adsorption - The step in the ion-exchange process that removes arsenate from water by chemical or physical attraction to a medium such as an ion exchange resin. It is also referred to as the service step or the exhaustion step. **Note:** In this document, the term adsorption is used in its general sense as a process for removing contaminants from a liquid by adsorbing them on a solid adsorbent by processes including ion-exchange, adsorption, and ligand exchange.

Anion - A negatively charged ion. The major anions of concern are divalent arsenate (HAsO_4^{2-}), monovalent arsenate (H_2AsO_4^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), and bicarbonate (HCO_3^-).

Anion Exchange Resin - A polymeric matrix, usually polystyrene crosslinked with divinylbenzene, containing fixed positively charged functional groups that hold exchangeable anions by electrostatic attraction. During an anion-exchange reaction, a harmless ion such as chloride is exchanged for a target contaminant ion such as arsenate (HAsO_4^{2-}).

Attrition - Breakage and wear of ion exchange resin beads.

Back Washing - The upward flow of water through an ion exchange bed to clean it of foreign material and reduce the compaction of the resin bed. Usually the bed is fluidized by the upward flow of water.

Bed - The ion exchange material contained in a column or vessel of an operating unit.

Bed Depth - The height of the resin material in the column after the exchanger has settled into a packed-bed condition.

Bed Expansion - The effect produced during backwashing: when the bed is fluidized, the resin particles become separated and rise in the column.

Bed Volumes (BV) or Bed Volumes Treated - A dimensionless ratio that refers to the volume of water that can be treated by a bed of resin. $\text{BV} = \text{Volume of water treated} / \text{volume of resin including voids}$.

Breakthrough - The portion of the effluent history curve that exhibits a rapid increase in effluent concentration of a substance, which signals that adsorption of the substance is near completion, and further operation of the column will not be productive. During plant operation, the adsorption cycle is terminated prior to breakthrough of the ion of interest. (The breakthrough point can be defined in several different ways such as the point on the breakthrough curve where the concentration of the target contaminant reaches the MCL or a predetermined fraction of the MCL, or where the inflection point in the breakthrough curve occurs. Breakthrough can be gradual or sharp depending on several factors including the isotherm shape, the resin particle size, mass transfer considerations, channeling in the bed, and etc.

Brine Recycle - The reuse of spent brine with or without treatment to remove the target contaminant, arsenic. Direct brine reuse, or brine recycling without treatment to remove arsenic, is possible during arsenic ion exchange because arsenate is removed as a divalent ion, HAsO_4^{2-} , undergoes electroselectivity reversal and is not attracted to the resin when it is in contact with high concentration brine.

Capacity - Generally, the advertised ion exchange capacity expressed in milliequivalents per milliliter or equivalents per liter. The number of equivalents of exchangeable ion contained in one

liter of an ion exchange material. The volume is measured when the material is wet and is fully saturated with adsorbed water.

Channeling - Random paths of relatively lower flow resistance in the resin bed resulting from improper operating procedures including failure to remove particulates, improper backwashing, insufficient flow velocity, etc. Channeling, which can occur during exhaustion or regeneration, results in diminished mass transfer between the water and the resin.

Chromatography - The separation of ions, molecular species, or complexes into highly purified fractions by means of ion exchange materials or adsorbents.

Chromatographic Peaking - The phenomenon that causes the effluent concentration of an ion to be higher than the influent concentration for a short time during the effluent history. Chromatographic peaking is also referred to as “dumping” and it occurs immediately following the breakthrough of each ion. All ions in the feed water are subject to peaking except the most-preferred ion, which is usually sulfate. During chromatographic peaking, significant amounts of the adsorbed ion are “dumped” from the resin bed into the effluent water.

Clumping - The formation of resin agglomerations in an ion exchange bed due to fouling, chemical depositions, scaling, or admixture with highly cohesive substances, such as certain clays and silts.

Column Influent -The water entering an ion exchange column or columns. Column influent water may have been subjected to pretreatment such as filtration or oxidant addition and, thus, may differ from feed water, which is the raw (source) water before pretreatment.

Column Operation - The most common method of employing ion exchange materials, in which the liquid to be treated passes through a fixed bed of ion exchange resin held within a cylindrical vessel or column.

Counter Flow Operation - An ion exchange operation in which the direction of flow of water through a bed and the subsequent regenerant flow are in opposite directions.

Cross-Linking - Connecting together at numerous points the linear polymer chains in the matrix of an ion exchange polymer using a bridging agent in order to produce a three-dimensional insoluble product. Lightly crosslinked resins are relatively more flexible, take up more water, and can absorb larger molecules more easily.

Cycle - A complete series of operational steps. For instance, a complete cycle of arsenate ion exchange would involve; the complete adsorption step, followed by backwashing, regeneration, slow rinsing, fast rinsing, and return to adsorption service.

Degradation - The physical or chemical reduction of ion exchange properties due to particulate fouling, organic fouling, chemical (including chlorine) oxidation, excessive heating and other

aggressive operating conditions. Some effects are bead cracking, capacity loss, particle size reduction, excessive swelling, or any combination of the above.

Divalent Ion - An ion with two negative charges such as sulfate, SO_4^{2-} , or arsenate, $\text{H}_2\text{AsO}_4^{2-}$

Down Flow - Conventional direction in which water and brines flow through an ion exchange bed during processing: inlet at the top, outlet at the bottom of the bed or column.

Dumping - The phenomenon that causes the effluent concentration of an ion to be higher than the influent concentration for a short time during the effluent history. Dumping is also referred to as “chromatographic peaking” and it occurs immediately following the breakthrough of an ion. All ions in the feed water are subject to peaking except the most-preferred ion, which is usually sulfate. During chromatographic peaking, significant amounts of the adsorbed ion are “dumped” from the resin bed into the effluent water.

Effluent - column effluent is the treated water leaving an ion-exchange column. Process effluent is synonymous with product or treated water, which can be the result of blending several column effluents together to smooth out water quality variations resulting from a single column. Process Effluent can also contain bypass water that has not been treated by ion exchange. The regenerant emerging from the column after regeneration is referred to as the eluent, eluate or spent regenerant.

Effluent History Curve- An x-y plot showing the relationship between time or bed volumes (BV) of water passed through a bed of ion-exchange resin (on the x-axis) and the effluent concentration (on the y-axis). Effluent concentration may be expressed as milliequivalents/L, mg/L, or the ratio $C_{\text{Effluent}}/C_{\text{Influent}}$. Contaminant breakthrough occurs when effluent history curve begins to rise sharply. The run is terminated at the breakthrough point when the effluent concentration reaches the MCL or some predetermined fraction of the MCL. Prior to contaminant breakthrough, the measurable amount of contaminant in the effluent history curve is referred to as leakage. As long as the leakage is below the predetermined MCL it is tolerable.

Elution - The stripping of adsorbed ions from the ion exchanger by the regenerant solution, which is usually highly concentrated, e.g., 1-2 molar NaCl (6-12% NaCl).

Electroselectivity Reversal - The reversal of selectivity, which occurs when the ionic strength of the aqueous solution is changed between natural water (low ionic strength, e.g., 0.005 M) and brine solution (high ionic strength, e.g., 1.0 M). Divalent ions such as sulfate and arsenate undergo selectivity reversal during regeneration and are easily stripped from the resin during regeneration, even though they are strongly attracted to the resin during exhaustion, which occurs in low ionic strength water.

Empty Bed Contact Time - The time it would take for water to pass through the volume of the column occupied by the resin bed. It is calculated as though the resin is not present, hence "Empty Bed" Contact Time. It is calculated as the volumetric flow rate divided by the resin bed

volume. For example if the flow rate is 350 gal/min and one Bed Volume is 700 gallons, the EBCT is 2 minutes (i.e., 2 min/BV or 0.5 BV/min, or 30 BV/hr).

Equivalent - Short for gram equivalent weight, the molecular weight of an ion divided by its ionic charge. One equivalent of ions contains Avagadro's number (6.023×10^{23}) of ionic charges. For example one equivalent (i.e., one gram equivalent weight = $139.9/2 = 69.95$ grams) of divalent arsenate (HAsO_4^{2-}) anions contains 6.023×10^{23} negative charges. Equivalents rather than grams of ions are used in ion exchange calculations because one equivalent of chloride ($35.5/2 = 17.75$ grams) is replaced by exactly one equivalent of arsenate (69.95 grams).

Exhaustion - That portion of the operating cycle during which the resin adsorbs (actually, removes by ion exchange) the contaminant from the raw water. The resin is spent or exhausted at the end of the exhaustion step.

Feed Water - Raw water from the source before pretreatment of any kind.

Fouling - Any deposit or concentration of foreign material on or in an ion exchange material which interferes with the chemical and physical processes. Typical foulants are: lubricating oil from pump lubricants, clays, silts, bacteria, algae, etc. Fouling can cause reduced efficiency, channeling, loss of resin during backwashing and many other plant malfunctions.

Freeboard - The space provided above the resin bed in a vessel or column to accommodate the expansion of the resin bed during the backwash cycle.

Headloss - The loss of liquid pressure head resulting from the passage of water through a bed of ion exchange material.

Hydraulic Loading Rate - Also referred to as the approach velocity (v_0) or the volume of water passing through a given area of resin within a given time. Hydraulic loading rate is usually expressed in terms of gallons per minute per square foot of bed cross sectional area. Hydraulic loading rate is not the same as the service flow rate (SFR), which is expressed as volumetric flow rate divided by resin bed volume, e.g., gal/min ft³.—For arsenic ion-exchange processes, these values are typically as follows: $v_0 = 10\text{-}15$ gal/min ft²; SFR = 3-5 gal/min ft³.

Influent - column influent is the raw, arsenic-contaminated water entering an ion exchange column. Column influent is not necessarily the same as the process influent, which is the feed water or raw water entering the process before any pretreatment. Column influent differs from feed water in that it may be filtered or oxidized and filtered, or otherwise subject to pretreatment before ion exchange.

Interstitial Volume - The space between the particles of an ion exchange material in a column or an operating unit (see Void Volume).

Leakage - The presence of the target contaminant (arsenate in this case) in the treated water exiting from an ion exchange column before its breakthrough has occurred giving the impression

that the contaminant has "leaked" through the resin bed. Leakage is different from breakthrough- the rapid increase in contaminant concentration, which occurs in the effluent history curve just before the run is terminated at the breakthrough point.

Milliequivalent (meq) - Short for one milligram equivalent weight, - one thousandth of an equivalent, i.e., 6.023×10^{20} ionic charges.

Monovalent Ion - An ion with a single negative or positive charge. Nitrate, NO_3^- , and chloride, Cl^- , are monovalent anions. Sodium, Na^+ , and hydrogen, H^+ , are monovalent cations.

Nitrate Selective Resin - Same as nitrate-to-sulfate selective (NSS) resin. An ion-exchange resin that prefers nitrate to sulfate even in low ionic strength waters (≤ 0.01 M). All resins are selective for nitrate over chloride, but may not be nitrate selective. Only special resins (NSS resins) are selective for nitrate over sulfate in the range of drinking water concentrations. Also, all resins are selective for nitrate over sulfate at brine concentrations (≥ 0.25 M). Because arsenate is adsorbed as a divalent ion (HAsO_4^{2-}) like sulfate, nitrate selective resins are generally not good for arsenic removal from drinking water.

Operating Cycle - A single completion of all steps in the exhaustion-regeneration process consisting of adsorption, backwash, regeneration, fast rinse, slow rinse, and, stand by.

Physical Stability - The ability of an ion exchange material to resist breakage caused by mechanical manipulation.

Presaturant - The harmless or innocuous ion adsorbed on the resin by saturating the resin with the ion prior to a column operation. In arsenate treatment, the presaturant is chloride ion.

Preferred Ion - The one of at least two different ions having equal concentrations that will be adsorbed on the resin to the greatest extent.

Recontamination - A potential problem in ion-exchange systems consisting of removing a contaminant from one point in a water supply and then adding the same and/or other contaminant into the supply at a different point. For example, by incomplete rinsing of resin beds, arsenate, nitrate, chloride, bicarbonate, sulfate and sodium can be added to the supply. Also, by running beds beyond their bed life, arsenate ion can be "dumped" from the bed into the treated water.

Regenerant - The solution (6-12% NaCl for arsenate removal) used to convert an ion exchange material from its exhausted state to the desired regenerated form for reuse.

Regeneration - Conversion of the spent resin back to the presaturant condition by elution of the contaminants after completion of the exhaustion and backwashing steps. In arsenate treatment, the regeneration is performed by passing a sodium chloride brine slowly through the bed in either a co- or countercurrent direction.

Regeneration Level - The amount of regenerant chemical used per unit volume of ion exchanger bed, commonly expressed as lb/ft³ or equivalents Cl⁻/equivalent resin. Also see salt loading. The lower the regeneration level, the more efficient is the process.

Resin - Synthetic organic ion-exchange materials, usually in bead form, with a large number ($\geq 6 \times 10^{23}$ sites/L resin) of charged ion-exchange sites within the hydrated solid. The typical strong-base anion (SBA) resins used in arsenate anion removal from water are divinylbenzene crosslinked polystyrene polymers with positively charged quaternary amine functional groups.

Resin Bed Volume - The volume of ion exchange resin material in a bed including voids between particles. The volume of the resin in the bed is referred to as one bed volume and is expressed in cubic feet, gallons, or liters.

Rinse - The passage of water through an ion exchange bed to wash out excess regenerant and residual contaminants. The slow rinse or displacement rinse is generally less than 3 BV and is performed at the same rate as the regenerant flow rate (0.5-1 gal/min ft³). The fast rinse is generally less than 20 BV, and is performed at the service (exhaustion) flow rate (3-5 gal/min ft³).

Run Length - The number of bed volumes (BV) or the exhaustion time (hrs) until the breakthrough point of the contaminant ion of interest, arsenic in this case. For arsenic removal we are interested in Run Length to Arsenic Breakthrough—RLTAsBT.

Salt Loading - Salt loading is the amount of regenerant applied to a resin during the regeneration step. It can be expressed in terms of pounds of NaCl per cubic foot of resin, grams of salt/L of resin, equivalents of salt/L of resin or, more conveniently, in terms of bed volumes of brine (volumes brine/ volumes resin) having a specified concentration of NaCl. Salt loading and regeneration level are equivalent terms.

7.0 TASK 1: SELECTION AND CHARACTERIZATION OF FEED WATER

7.1 Introduction

The Manufacturer must choose either a surface or ground water location to test the ion exchange plant. Generally, a ground water would be chosen because most of the drinking water arsenic problems will be associated with ground waters. On the other hand, if the target market is surface waters, a surface water test site should be chosen because ground water testing may not fully challenge the plant. For example, surface waters will contain higher TOC and particulates, and be subject to significant seasonal variations in temperature, arsenic concentration, algae, turbidity, color, taste and odor, and TOC.

When removing arsenic from water by anion exchange, sulfate present in the water will reduce the capacity of the resin for arsenic. For example, sulfate in excess of 200 mg/L may rule out the ion-exchange process entirely, because run lengths may be less than 250 BV, which some consider to be the lower limit for a practical ion-exchange process for public water supply treatment.

Therefore, care should be taken during verification testing to use waters with similar sulfate levels to those expected to be encountered during full scale operation. See Section 2.2.1 - “Effect of Sulfate on Arsenic Removal”. If it is the objective of the manufacturer to prove that their unit is widely acceptable for arsenic removal from ground water, test waters with very low sulfate concentration, e.g., less than 20 mg/L, should be avoided. If a manufacturer chooses to demonstrate the effectiveness of their plant under a significantly different set of background water conditions, the option exists for a second test period to be carried out at a different site with the same transportable ion-exchange plant.

7.2 Objectives

The first objective of this task is to choose a representative site with water quality and water quality variations that will be similar to locations where the ion exchange process will be implemented. Once the site has been chosen, the second objective is to fully characterize the feed water with respect to the chemical, particulate, and biological parameters that would be expected to influence the ion-exchange process performance.

7.3 Work Plan

This selection and characterization task can be accomplished by using analytical measurements obtained from third party sources (i.e. United States Geological Survey (USGS), USEPA, State Laboratories, and Municipal Laboratories). If sufficient water quality data for the site do not exist, they must be generated by the Manufacturer using at least three sets of samples taken over a period of at least one month or more, during which time the water source is in operation as it would be during Verification Testing. The new data will be included in the Field Operations Document. The specific parameters and approved methods needed to characterize the water are listed in the Table 2 below:

Sufficient information shall be obtained to illustrate the variations expected to occur in these parameters that will be measured during Verification Testing for a typical annual cycle for the water source. This information will be compiled and shared with NSF so NSF and the Field Testing Organization can determine the adequacy of the data for use as the basis to make decisions on the testing schedule. Failure to adequately characterize the feed water (source water) could result in testing at a site later deemed inappropriate, so the initial characterization will be important to the success of the testing program. Clifford (1990 Chapter 9) has shown that the sulfate concentration in the raw water is a primary determinant of arsenic run length, and Ghurye and Clifford (1998) have recently demonstrated that nitrate peaking before arsenic breakthrough may determine the ion exchange run length.

The presence of iron above about 0.3 mg/L in a ground water will influence the process design. First, significant iron will signal a reducing water with As(III) the predominant species present, and the As(III) must be oxidized to As(V) prior to ion exchange treatment. Second, when exposed to the air, which inevitably occurs during treatment, some ferrous iron will be oxidized to ferric and will form a precipitate, which may adsorb significant arsenic. Research (Ghurye and Clifford, 1998) has shown that the precipitated iron will largely pass through the anion resin and

cause high arsenic in the column effluent. Thus, iron above about 0.3 mg/L should be removed by oxidation and precipitation prior to anion exchange. When this situation occurs, one should consider a coagulation-filtration or a coagulation-microfiltration process rather than ion exchange for arsenic removal.

Table 2. Historical Water Quality Data

Ground Water	Surface Water	Standard Method	EPA Method
As(III) and As(V)	As(III) and As(V)	Methods for analyzing As(III) and As(V) are non-standard.	
Total As	Total As	3500-As, 3113 B, 3120 B, 3114 B	200.7, 200.8, 200.9
Sulfate	Sulfate	4500-Sulfate, 4110 B	300.0, 375.2
Nitrate	Nitrate	4500-NO ₃ , 4110 B	300.0, 353.2
Chloride	Chloride	4500-Cl ⁻ D, 4110 B	300.0
Total Alkalinity	Total Alkalinity	2320-B	
Fluoride	Fluoride	4500-F, 4110 B	300.0
pH	pH	4500-H ⁺ B	
TDS	TDS	2540-C	
TOC	TOC	5310-C	
Temperature	Temperature	2550-B	
Iron		3111 B, 3113 B, 3120 B	200.7, 200.9
Manganese		3111 B, 3113 B, 3120 B	200.7, 200.8, 200.9
	Color	2120-B	
	Turbidity	2130-B	180.1
	Algae	10200 and 10900	

If the source water is surface water, a brief description of the watershed that provides the feed water shall be provided to aid in predicting water quality variability and characterizing the feed water. The watershed description should include:

- (1) approximate size,
- (2) topography (i.e. flat, gently rolling, hilly, mountainous),
- (3) types of human activities that take place (i.e. mining, manufacturing, cities or towns, farming),
- (4) potential sources of pollution influencing water quality, especially potential sources for arsenic discharge, and
- (5) nature of the water source, such as stream, river, lake, wells, or man-made reservoir.

A primary consideration when using anion exchange to treat surface water is the natural organic matter (NOM), measured as TOC, present in the source water. Because a significant portion of the NOM comprises large anions with aromatic character and multiple negative charges, some NOM will be irreversibly adsorbed by the resin and may eventually lead to organic fouling

(Clifford et. al., 1998, TOC IX Chapter in DBP Book). To clean the resins, a regenerant mixture of NaOH and NaCl will occasionally be used, and this complicates the process significantly. Thus, anion exchange for removing arsenic from surface water will not be commonly applied, but is sometimes used. For example, chloride anion exchange for nitrate removal, which is very similar to arsenate removal, has been installed in Des Moines, Iowa, to remove nitrate from the Des Moines river water. This process has been reported to be successful and serious organic fouling has not occurred (Benjamin, Des Moines, IA, 1998). For surface water treatment, the test plan must include the season with the highest expected TOC values, and a sufficient number of ion exchange runs must be made so that conclusions about the potential for organic fouling may be made. Alternatively, the manufacturer may provide resin testing data on the water to be treated that indicates that serious fouling will not occur during the projected life of the resin.

7.4 Schedule

In many cases, sufficient water quality data may already exist such that the determination of the suitability of a source water for use as feed water in an ion-exchange process Verification Testing program might be made without further testing. If historical data is insufficient, sampling and analysis of the proposed test water must be undertaken. As a minimum, the water should be sampled three times over a period of one month to characterize one test period. If the water is expected to vary from season to season, e.g., a surface water, one additional test period must be defined and characterized.

7.5 Evaluation Criteria

Feed water quality will be evaluated in the context of the Manufacturer's statement of performance capabilities. The feed water should challenge the capabilities of the equipment but should not be beyond the range of water quality suitable for treatment for the equipment in question. For example, if the Manufacturer's equipment is designed for source water containing less than 500 mg/L TDS, and 200 mg/L sulfate, it would not be appropriate to test it on waters with greater than these levels of TDS and sulfate.

Because the ion exchange breakthrough point of a trace-level contaminant will not be significantly affected by its concentration, the arsenic level in the raw water will generally not be a determinant of process success or failure. Nevertheless, because increasing the feed water arsenic level will lead to proportionately higher arsenic leakage, it would not be reasonable to spike the feed water with more than the highest expected level of arsenic in the waters to be treated. The minimum arsenic level in the test water should be the lesser of 20 µg/L or three times the applicable EPA-specified MCL.

If the manufacturer wants to claim As(III) removal, the unit must be challenged with an As(III)-containing test water, otherwise an As(V) challenge water will be acceptable. When challenging the unit with As(V), sufficient chlorine or an alternative oxidant may be added to the water to insure the oxidation of any As(III) present to As(V).

8.0 TASK 2: PREPARATION, COORDINATION, AND STARTUP

8.1 Introduction

One or more meetings will be held regarding the tasks and scheduling of tasks between the manufacturer and the NSF-approved testing organization regarding the tasks described in the NSF approved manufacturer's FOD. This task will also include the plant start up if it is not already in operation. If possible, the Manufacturer and the Field Testing Organization representative(s) should be present together during the plant start up for purposes of training the testing personnel in plant operation and maintenance.

8.2 Objective

The objective of the meeting(s) is to train the Field Testing representative(s) to operate the plant and to provide an opportunity for the Manufacturer and the Field Testing Organization personnel to reach a common understanding of the objectives and execution of the testing plan. Further, the meeting(s) will provide an opportunity to clarify any areas of concern by either party. Initial start up data may be collected if the plant is not already in operation. Other interested parties such as the owner/operator and local or state health officials should attend at least a portion of the meeting.

8.3 Work Plan

The Manufacturer will explain the material included in the FOD; in particular, the plant design, operations, outstanding and distinguishing features and especially the treatment objectives and other secondary performance goals claimed for the plant performance.

The treatment objectives shall include the following:

- (1) The process effluent shall always meet the MCL for arsenic.
- (2) The process effluent pH shall be within the specified design range (typically 7.0-9.0).
- (3) The process effluent nitrate-N shall never exceed 10 mg/L.
- (4) No primary MCL shall be exceeded by the process effluent.
- (5) The volume of wastewater, including brine and rinses, discharged from the process shall be equal to or less than the Manufacturer's claims (typically $\leq 2\%$ of product water volume).
- (6) The regenerant salt consumption, e.g., lbs NaCl/1000 gal product water, shall meet the Manufacturer's claims (typically ≤ 3 lbs/1000 gal). The Manufacturer will also report the resin-regeneration salt loading in the units of lbs regenerant/ft³ resin.
- (7) The arsenic concentration of the wastewater shall meet all wastewater regulations applicable to the specified method of disposal.
- (8) Arsenic sludges produced by the process shall meet applicable regulations for disposal.

The Manufacturer will use diagrams, drawings, plans and the actual equipment to illustrate the design, operation and control of the ion-exchange system being tested. Special attention will be given to critical equipment such as alarms, controls, and safety devices. Emergency shut down procedures will be carefully reviewed.

8.4 Schedule

Prior to the meeting(s), the Manufacturer will provide the Testing Organization with any drawings, plans, site plans, operation manuals, and similar helpful materials. Sufficient time should be allowed prior to the meeting to allow the testing organization to develop their testing plans and methods to quantify the evaluation criteria. The orientation meeting(s) will be held just before the next task: Initial Plant Characterization.

9.0 TASK 3: INITIAL PLANT CHARACTERIZATION

9.1 Introduction

Shortly after the orientation and training meetings between the Manufacturer and the Testing Organization, Initial Plant Characterization Tests will be conducted by the Field Testing Organization or the Manufacturer and the base line performance data will be recorded. During these tests, a preliminary assessment of plant performance will be made. If the plant doesn't perform to specification, adjustments can be made prior to the actual Verification Testing. Furthermore, the performance data obtained during these preliminary tests will provide base line data for comparison with future plant performance. When Verification Testing is complete, a comparison between the early and late plant performance can be made to determine if performance has deteriorated over time.

This Initial-Plant-Characterization-Test phase is a logical time for NSF to carry out a field inspection of equipment operations and sampling and field analysis procedures. If problems are found with the operation and/or data collection procedures, they may be corrected before the Verification Testing begins. Also, these preliminary test results should be reported to the Manufacturer, which may choose to make NSF-approved changes in operating procedures prior to Verification Testing.

9.2 Objective

The objectives of this task are to establish the initial plant performance characteristics and to permit NSF and the Manufacturer to make approved changes in the FOD prior to Verification Testing. The approved preliminary data may be used as base-line data for comparison with future plant performance.

9.3 Work Plan

9.3.1 Arsenic Spiking

If there is insufficient arsenic naturally present in the feed water, spiked arsenic may be used at a concentration sufficient to permit the most-stressed operation claimed by the Manufacturer. The minimum arsenic level in the test water should be the lesser of 20 µg/L or three times the applicable EPA-specified MCL. If the manufacturer wants to claim As(III) removal, the unit must be challenged with an As(III)-containing test water, otherwise an As(V) challenge water will be acceptable. When challenging the unit with As(V), sufficient chlorine or an alternative oxidant may be added to the feed water to insure the oxidation of any As(III) present to As(V). When spiking the feed water, the following guidelines are suggested:

- (1) Arsenic spiking of the feed water shall begin at least 24 hours prior to any actual data collection so that the spiking system is at steady state and has stabilized.
- (2) Arsenic (III) feed solution will be prepared by diluting the arsenic into dilution water that is distilled or deionized and oxidant free. Arsenic (V) feed solution will also be prepared in distilled or deionized water, which may contain an oxidant.
- (3) To spike arsenic (III), use Analytical Reagent Grade sodium arsenite, NaAsO_2 .
- (4) To spike arsenic (V), use Analytical Reagent Grade sodium arsenate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$.
- (5) The feed reservoir for the arsenic spike solution shall be made of chemically inert material such as polyethylene, polypropylene, or stainless steel, which will not adsorb arsenic.
- (6) The reservoir will be mixed continuously throughout the experiment.
- (7) The arsenic spike solution will be fed using an adjustable rate chemical feed pump.
- (8) Use an in-line static mixer or a rapid mixing chamber to mix this solution into the feed water.

If Manufacturers wish to prove that their process will oxidize and remove As(III), spiking with As(III) will be necessary. When feeding As(III) to a plant, Manufacturers and Field Testing Organizations need to be aware of potential difficulties in preventing conversion of As (III) to As (V) as the spiking solution is held in its storage container. Further conversion to the higher valence state could occur during passage of spiked water through the package plant. This is very significant because As(III) is not removed by chloride anion exchange (Clifford et. al. 1998). Thus, pre-oxidation to convert As(III) to As (V),

with an oxidant such as free chlorine is mandatory if As(III) is present at levels near or above the MCL for total arsenic (Frank and Clifford, 1986).

9.3.2 Attainment of Steady State Operation

The recording of data for the Initial Plant Characterization Tests should begin only after the arsenic ion exchange plant has reached steady state operation, which occurs when the mass of arsenic removed by the resin equals the mass of arsenic eluted from the resin during regeneration. The acceptable QA/QC error range for arsenic analysis and flow rate measurements will determine the acceptable range of error for the mass balance on arsenic. For arsenic removal, steady state should be reached within 3-5 exhaustion-regeneration cycles because arsenic is easily eluted from the resin during regeneration. To first set the controls on the system, an estimate of arsenic run length may be obtained from small-column lab data or by using predictive equations based on equilibrium multicomponent chromatography theory (Clifford, 1995; Tirupanangadu, 1997; Guter, Cathedral Peak Software Computer Program.).

Balancing the arsenic adsorbed with that eluted during regeneration may be accomplished as follows: Calculate the mass of arsenic adsorbed by measuring the area between the influent and effluent arsenic curves. Measure the mass of arsenic eluted during regeneration by sampling and analyzing the composite sample of collected regenerant and rinse waters.

In the event that a single ion-exchange column exhaustion cycle would require more than 2,000 BV to exhaust a column on the water to be tested, steady state will be defined as the completion of three exhaustion-regeneration cycles of at least 2,000 BV. For systems with multiple parallel columns operating simultaneously, this rule shall apply to each operating column in the system, i.e., each column must be subjected to three exhaustion-regeneration cycles of at least 2,000 BV. A carousel system will be defined as having reached steady state when all the following conditions have been met: (a) at least three rotations have been completed, (b) the regenerant mass and volumetric flow rates have been stable ($\pm 25\%$) for two days, and (c) the effluent concentrations of the target contaminants, e.g., arsenic, and nitrate have been stable ($\pm 25\%$) for two days.

Note: The Verification Testing Runs must be performed at the same operating conditions that were used to define steady state operation during the Initial Plant Characterization Tests.

9.3.3 Collection of Preliminary Data

Feed and Product Water Analyses: At least two feed water (raw water) and 10 product water (process effluent water) samples should be collected and analyzed during the preliminary exhaustion runs. It is recommended that complete preliminary data be collected for at least one Initial Characterization run, which shall consist of at least one exhaustion-regeneration cycle for each column in the operating system. For a two-column

system with one column designed to be operating while a second column is in standby mode, the Initial Characterization Run would consist of only one exhaustion-regeneration cycle. For a four-column system designed to have three columns operating in parallel at different stages of exhaustion while a fourth column is in standby mode, the Initial Characterization Run would consist of three exhaustion-regeneration cycles. The samples should be appropriately labeled as to Run No., Cycle No., BV and sampling time. Ground waters and surface waters should be analyzed for pH, arsenic, nitrate, sulfate, chloride, and bicarbonate according to the methods listed in Table 1.

Operating Data: The following operating data should be recorded by time of day during the preliminary run(s):

- (1) controller set points for each bed including:
 - flow rate of product water,
 - start time, finish time, and volume to exhaustion,
 - flow rate and volume of backwash water,
 - mass of salt and volume of regenerant used for each regeneration,
- (2) pressure readings for each column and pre-filter device
- (3) number of vessels in exhaustion, regeneration, and standby
- (4) visual observations of piping leaks, scaling and fouling problems, resin condition

9.3.4 Determination of Variable Effluent Quality and Arsenic Peaking Potential

Effluent Histories: For systems that operate with only one or two ion-exchange columns in service at a time, concentration vs. bed volume plots (effluent histories) should be plotted on the same graph for pH, arsenic, nitrate, sulfate, chloride and bicarbonate. At least one complete set of effluent history curves (≥ 6 data points for each curve) for one column should be plotted during the Initial Plant Characterization Tests. It is not necessary to plot the single-column effluent histories if the system consists of three or more multiple parallel columns, operating simultaneously.

Arsenic Peaking Potential: The potential for arsenic peaking should be determined to quantify the danger of exceeding arsenic breakthrough when only one or two simultaneously exhausted columns are employed for arsenic treatment. The arsenic peaking potential can be determined during the construction of the effluent history curves by running the column to a point 500 BV beyond the known breakthrough point for arsenic. Collect at least 10 samples for arsenic analysis at appropriate intervals, especially just before and after the anticipated arsenic breakthrough point, so that an effluent history can be constructed showing the arsenic peak that would occur if the run is not terminated at the proper time.

9.3.5 Preliminary Assessment of Plant Performance:

The preliminary data collected during the Initial Plant Characterization Tests should be summarized and analyzed by the Field Testing Organization and reported to the Manufacturer and NSF. If the plant doesn't meet its performance objectives, the tests may be re-run with improved operating conditions as approved and/or suggested by the Manufacturer. Alternatively, the Manufacturer may wish to cancel the remainder of the Verification Testing program. If there are no significant problems with the performance data and no objections to the preliminary testing procedures, the Verification Testing may proceed as planned. If problems arise, they must be resolved to the satisfaction of NSF before Verification Testing begins.

9.4 Schedule

Task 3, the Initial Plant Characterization Tests will be performed as soon as possible after Task 2, Preparation, Coordination and Startup. Unless the arsenic run lengths are exceptionally long ($\geq 2,000$ BV), steady state operation should be achieved within one week after starting the preliminary tests. For a three-parallel-column system operating at 2,000 BV run length, steady state should be achieved within 10-12 days. The collection of preliminary data and the arsenic peaking tests should be completed within two more weeks and the preliminary assessment of plant performance should take no more than one week. Thus, one month should be sufficient for the Initial Plant Characterization Tests.

10.0 TASK 4: VERIFICATION TESTING RUNS

10.1 Introduction

This task, which comprises the actual Verification Testing Runs, is the core of the Verification Testing Plan. During this task, the arsenic-removal ion exchange plant shall be operated for at least 240 hours over a period of at least 14 days during one testing period to collect data on equipment performance and water quality for purposes of performance verification. If a manufacturer chooses to demonstrate the effectiveness of their plant under a significantly different set of background water conditions, the option exists for a second test period to be carried out at a different site with the same transportable ion-exchange plant.

10.2 Objectives

The objectives of the Verification Testing Runs are to (a) to observe and record the plant operating conditions and equipment performance, (b) determine the overall feed water and finished water quality, and (c) establish the arsenic-removal performance of the plant.

10.3 Work Plan

10.3.1 Plant Operating Conditions and Equipment Performance

If the package water treatment equipment is being used for production of potable water and treats a water that naturally contains concentrations of arsenic appropriate for Verification Testing, so that arsenic spiking is not needed, routine operation for water production is anticipated in the time intervals between verification runs. The operating and water quality data collected and furnished to the Safe Drinking Water Act (SDWA) primacy agency during these times shall also be supplied to the Field Testing Organization.

The plant shall be operated for at least 240 hours during a period of 14 days or longer using the set point conditions determined in the Initial Plant Characterization Tests.

Table 3 indicates the operating and performance data to be collected during the Verification Testing Runs.

10.3.2 Feed Water and Product Water Quality

Water Quality Measurements: Water quality data shall be collected for the feed water, column influent water, and product water, as shown in Table 4, during Verification Testing. At a minimum, the required sampling schedule shown in Table 4 shall be observed by the Field Testing Organization. Water quality goals and target removal goals for the water treatment equipment shall be recorded in the Field Operations Document in the statement of capabilities.

Some of the water quality parameters described in Table 4 will be measured on-site by the Field Testing Organization (see Table 5). Analysis of the remaining water quality parameters will be performed by a state-certified or third party or EPA-accredited analytical laboratory. The methods to be used for measurement of water quality parameters in the field are described in Table 5. The analytical methods utilized in this study for on-site monitoring of feed water and filtered water qualities are discussed in Task 6, Quality Assurance/Quality Control (QA/QC).

Table 3. Operating and Performance Data from Verification Test Runs	
Parameter	Frequency
For the Entire Plant	
Instantaneous product water flow rate, gpm	Twice daily
Cumulative product water flow rate, gal	Twice daily
Cumulative waste water flow, gal	Daily
Brine consumption, gal	Daily
NaCl consumption, lbs and lbs/1000 gal product water	Daily
^{&} Volume of arsenic-contaminated sludge, gal	Daily
^{&} Solids conc. of arsenic-contaminated sludge, wt% solids	Daily
^{&} Mass of arsenic contaminated sludge, lbs	Daily
[†] Diluted brine concentration, wt% NaCl	Daily
[†] Brine flow rate, gpm	Twice Daily
[†] Average time in exhaustion zone, hrs & BV of feed water	Daily
[†] Average time in regeneration zone, hrs & BV of regenerant	Daily
[†] Average time in rinse zone, hrs & BV of rinse water	Daily
[†] Carousel rotation time, hrs	Daily
Number of columns exhausted	Daily
Number of columns regenerated	Daily
Electrical energy consumption, kwhr	Daily
Energy cost, \$/day	Daily
Equipment malfunctions, description of each malfunction and its result on plant performance.	As they occur
For Each Column in a Fixed-Bed Plant	
Instantaneous feed water flow rate, gpm	Twice daily
Pressure drop, psig	Twice daily
Cumulative feed water flow, gal	Daily
Exhaustion start and stop times, time of day	Each exhaustion
Regeneration start and stop times, time of day	Each regeneration
Displacement rinse start and stop times, time of day	Each rinse
Brine consumption, gal	Each Regeneration
Brine flow rate, gpm	Daily
NaCl consumption, lbs	Each Regeneration
^{**} Diluted brine concentration, wt% NaCl	Daily
Visual inspection of resin level through site glass	Daily
^{&} Only those plants with Fe(III) precipitation of brine will produce a sludge to be disposed of. Some plants will not produce an arsenic sludge.	
[†] For a carousel plant	
^{**} If more than one dilution device exists in a plant, each device will be sampled and analyzed daily.	

Table 4. Water Quality Sampling and Measurement Schedule	
<u>Parameter</u>	<u>Minimum Frequency*</u>
pH	Continuous Monitoring of feed water and product water, daily on-site verification
Conductivity	Continuous Monitoring of product water, daily on-site verification
TDS	Daily on composite samples of feed water and product water
[¶] Residual Cl ₂	Once per six hours on column inlet water, daily composite on product water
[†] Arsenic, Total	Once per six hours on product water, daily composite on feed water
§Arsenic(III)	At least four times on column inlet water during the course of the verification testing runs.
[†] Sulfate	Daily on composite samples of feed water and product water
[†] Nitrate	Daily on composite samples of feed water and product water
[†] Chloride	Daily on composite samples of feed water and product water
[†] Total Alkalinity	Daily on composite samples of feed water and product water
*All the above measurements assume a multiple column plant with at least three columns operating simultaneously, or a carousel plant. For one or two columns operating singly or in parallel, more frequent water quality analyses will be required because the water quality will be more variable. See note [†] below.	
[¶] If another oxidant is used, the residual concentration of that oxidant should be measured.	
[†] In addition to the daily composite samples, when one or two columns is operating singly or in parallel, the product water during one complete exhaustion cycle of at least one column must be analyzed once per 50 bed volumes based on the volume of resin in service at any given time. For an EBCT of 1.5 min, a 50 BV frequency translates to one sample per 75 min.	
§As(III) speciation will only be required when claims are made regarding the ability of the plant to remove As(III). The assessment of arsenic-removal performance shall not be dependent on the form of arsenic fed to the plant. Regardless of whether As(III) or As(V) or a mixture of the two is fed, the performance requirements will be determined by the measurement of As(total) in the product water. For purposes of determining the reasons for high arsenic in the product water, the Manufacturer and the Field Testing Organization are encouraged to measure the As(III) concentration in the product water whenever the MCL is closely approached or exceeded.	

Water Quality Sample Collection: Water quality data shall be collected during each of the specified periods of Verification Testing. Before the any data is collected, the plant must have reached steady state, which has been previously defined in Section 9.3.1. Additional sampling and data collection may be performed at the discretion of the Manufacturer. Sample collection frequency and protocol shall be defined in the Field Operations Document.

In the case of water quality samples that will be shipped to the state-certified or third party or EPA-accredited analytical laboratory for analysis, the samples shall be collected in appropriate containers (containing preservatives as applicable) prepared by the state-certified or third party or EPA-accredited, analytical laboratory. These samples shall be

preserved, stored, shipped and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical laboratory.

Table 5. Analytical Methods			
Parameter	Analysis Location	Standard Method	EPA Method
Arsenic concentration	Lab	3500-As, 3113 B, 3114 B, 3120 B	200.7, 200.8, 200.9
Arsenic species	Field	Modified anion exchange method for field speciation. ^a	
pH	On-Site	4500-H ⁺	
Conductivity	On-Site	2510-B	
Sulfate	On-Site or Lab	Test Kit 4500-Sulfate, 4110 B	300.0, 375.2
Chloride	On-Site or Lab	Test Kit or Electrode 4500-Chloride, 4110 B	300.0
Total alkalinity	On-Site or Lab	Test Kit-Digital Titrator 2320-B	
Nitrate	On-Site or Lab	Test Kit 4500-Nitrate, 4110 B	300.0, 353.2
Total organic carbon ^b	Lab	5310-C	
Turbidity ^b	On-Site or Lab	2130-B	180.1
Iron	On-Site or Lab	Test Kit 3111 B, 3113 B, 3120 B	200.7, 200.9
Manganese	On-Site or Lab	Test Kit 3111 B, 3113 B, 3120 B	200.7, 200.8, 200.9
^a Methods for analyzing As(III) and As(V) are non-standard but the modified anion exchange method for field speciation as described in Edwards et al., 1999, may be used or another method may be submitted to NSF for consideration. ^b Turbidity and TOC measurement will only be required for surface waters or unusual ground waters. When turbidity is a problem, pressure prefiltration will be employed as a pretreatment for ion exchange.			

10.3.3 Arsenic Removal Performance

Arsenic removal will generally be the purpose for installing and operating the ion exchange plant. However, some nitrate- or uranium-removal ion-exchange plants might

also be tested for arsenic removal. In the latter cases, the performance of the plant will be determined on meeting all applicable SDWA MCL criteria and additional performance claims made by the Manufacturer. This section of the Verification Testing Plan deals only with the requirements for meeting the SDWA MCL and additional performance Manufacturer claims related to arsenic removal.

Evaluation of arsenic removal shall be performed by analyzing arsenic in the feed and product waters, and in the blended water if applicable. If arsenic spike testing is required, the feed water arsenic measurement will be made after appropriate arsenic species—either arsenate (As(V)) or arsenite (As(III))—have been added to the feed water. If arsenic spiking of feed water is employed, the ion-exchange system with spiking should have been tested and have reached steady state operation during the Initial Plant Characterization Tests (see Task 3, Section 9.3.1). Arsenic sampling and analysis shall be performed as specified in Table 5.

Arsenic Sample Collection: Water quality data shall be collected during each of the specified periods of Verification Testing. Before the any data is collected, the plant must have reached steady state, which has been previously defined as five exhaustion-regeneration cycles for each column in the fixed bed or carousel system.

10.4 Schedule

The plant shall be operated for at least 240 hours during a period of 14 days or longer using the set point conditions determined in the Initial Plant Characterization Tests. **Note:** According to the initial plant characterization tests, the longest run length will be 2,000 BV. At a typical EBCT of 1.4 minutes (1000 BV/day), the exhaustion of a column will require 48 hours, thus, at least five exhaustion-regeneration cycles for each column in an operating system will be completed during the 240-hour Verification Test Period.

10.5 Evaluation Criteria

Performance of ion exchange package plants shall be evaluated in the context of the Manufacturer's statement of performance capabilities with respect to (1) treatment equipment performance, (2) finished water quality, and (3) arsenic removal performance.

10.5.1 Treatment Equipment Performance

The goal of this sub-task was to operate the plant within the mechanical, electrical, and cost constraints for at least 240 hours during the Verification Testing Runs. To pass the Treatment Equipment Performance test, the plant must meet all the criteria specified in the FOD. These would include criteria such as (1) advertised capacity in terms of total daily treated water production, waste water discharges, sludge production, NaCl consumption, electrical costs, maintenance costs, total cost of treatment in terms of \$/1000 gallons product water, and other relevant equipment performance criteria.

10.5.2 Product Water Quality

Because an ion-exchange bed produces a variable water quality as it is exhausted, care must be exercised to ensure that the variable effluent quality doesn't violate the finished water quality criteria at any time. For example, the effluent pH may be lower than 7.0 during the early portions of a run. This variable water quality problem is generally addressed by simultaneously operating three or more columns in parallel or by using a carousel system. To pass the Product Water Quality test, at least 95% of the product water samples must be within the pH range of 7.0-9.0 and have a nitrate concentration below the MCL, in addition to meeting the MCL for arsenic and all other applicable MCLs.

10.5.3 Arsenic Removal Performance

A properly operated ion exchange process can easily achieve an effluent arsenic concentration below 1.0 µg/L, a level below any likely MCL adopted by EPA. However, if the resin is not rinsed properly following regeneration or if the column is allowed to run beyond breakthrough, arsenic MCL violations might occur. To pass the Arsenic Removal Performance criteria, the plant must consistently deliver a finished water which is below the arsenic MCL, i.e., 95% of the product water samples must be below the arsenic MCL. Furthermore, no product water samples may exceed the feed water concentrations of arsenic (total) or nitrate.

The assessment of arsenic-removal performance shall not be dependent on the form of arsenic fed to the plant. Regardless of whether As(III) or As(V) or a mixture of the two is fed, the performance requirements will be determined by the measurement of As(total) in the product water. For purposes of determining the reasons for high arsenic in the product water, the Manufacturer and the Field Testing Organization are encouraged to measure the As(III) concentration in the product water whenever the MCL is closely approached or exceeded.

11.0 TASK 5: DATA MANAGEMENT

11.1 Introduction

The data management system used in the verification testing program shall involve the use of computer spreadsheet software and manual recording of operational parameters for the water treatment equipment on a daily basis.

11.2 Objectives

The objective of this task is to establish a viable structure for the recording and transmission of field testing data such that the Field Testing Organization provides sufficient and reliable operational data for the NSF for verification purposes. A second objective is to develop a statistical analysis of the data, as described in "Protocol for Equipment Verification Testing for Arsenic Removal."

11.3 Work Plan

11.3.1 Data Handling

SCADA Systems: The following protocol has been developed for data handling and data verification by the Field Testing Organization. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases.

- (1) Specific parcels of the computer databases for operational and water quality parameters should be downloaded by manual importation into Excel (or similar spreadsheet software) as a comma delimited file.
- (2) Specific database parcels will be identified based on discrete time spans and monitoring parameters.
- (3) The data will be manipulated into a convenient framework to allow analysis of ion-exchange equipment operation in a spreadsheet form.
- (4) Backup of the computer databases to diskette should be performed on a monthly basis at a minimum.

Non-SCADA Systems: In the case when a SCADA system is not available:

- (1) Field testing operators will record data and calculations by hand in laboratory notebooks. (Daily measurements will be recorded on specially-prepared data log sheets as appropriate.)
- (2) Laboratory notebook will contain carbon copies of each page (to ease referencing the original data and offer protection of the original record of results).
- (3) Original notebooks will be stored on-site; the carbon-copy sheets will be forwarded to the project engineer of the Field Testing Organization at least once per week.
- (4) Pilot operating logs shall include a description of the process equipment (description of test runs, names of visitors, description of any problems or issues, etc.); such

descriptions shall be provided in addition to experimental calculations and other items.

Spreadsheets:

- (1) The data for the project will be recorded in custom-designed spreadsheets.
- (2) The spreadsheets will be capable of storing and manipulating each monitored water quality and operational parameter from each task, sampling location, and sampling time.
- (3) All data from the laboratory notebooks and data log sheets will be entered into the appropriate spreadsheet.
- (4) Data entry will be conducted on-site by the designated field testing operators, with all recorded calculations checked at this time.
- (5) Following data entry, the spreadsheet will be printed out and the printout will be checked against the handwritten data sheet.
- (6) Any corrections will be noted on the hard-copies and corrected on the screen, and a corrected version of the spreadsheet will be printed out.
- (7) Each step of the verification process will be initialed by the field testing operator or engineer performing the entry or verification step.

Data Tracking:

- (1) Each experiment (e.g., each ion-exchange test run) will be assigned a run number which will then be linked to the data from that experiment through each data entry and analysis step.
- (2) Data will be tracked by use of the same system of run numbers as samples are collected and sent to state-certified or third party or EPA-accredited analytical laboratories.
- (3) Data from the analytical laboratories will be received and reviewed by the Field Testing Organization.
- (4) These data will be entered into the data spreadsheets, corrected, and verified in the same manner as the field data.

11.3.2 Statistical Analysis

Arsenic data developed from grab samples collected during filter runs according to the Analytical Schedule in Task 4 of this Test Plan shall be analyzed for statistical uncertainty. The Field Testing Organization shall calculate 95% confidence intervals for the arsenic data obtained during Verification Testing as described in "Protocol for Equipment Verification Testing for Arsenic Removal." A separate statistical analysis shall be carried out for each testing condition for which the required 11 or more sets of arsenic samples were collected and analyzed.

The statistics developed will be helpful in demonstrating the degree of reliability with which the water treatment equipment can attain quality goals under the treatment conditions tested. The results of the statistical analysis also shall be used to determine if the performance of the equipment was equal to or better than that given in the statement of performance capabilities.

12.0 TASK 6: QUALITY ASSURANCE/QUALITY CONTROL

12.1 Introduction

Quality assurance and quality control (QA/QC) of the operation of the ion exchange equipment and the measured water quality parameters shall be maintained during the Verification Testing program.

12.2 Objectives

The objective of this task is to maintain strict QA/QC methods and procedures during the Equipment Verification Testing Program. Maintenance of strict QA/QC procedures is important, in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to verify exact conditions at the time of testing.

12.3 Work Plan

Equipment flow rates and associated signals should be verified and recorded on a routine basis. A routine daily walk-through during testing will verify that each piece of equipment or instrumentation is operating properly. Particular care will be taken to verify the water, brine, and arsenic spiking (if applicable) flow rates are correct. In-line monitoring equipment, such as flow meters and conductivity meters, will be checked to verify that the readout matches with the actual measurement (i.e. flow rate, specific conductance) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods.

12.3.1 Daily QA/QC Verifications

The product water pH meter should be checked and calibrated daily.

The following parameters should be verified by weight or by volume:

- (1) Chlorine or oxidant consumption
- (2) NaCl consumption
- (3) Concentrated arsenic spiking solution flow rate
- (4) Saturated brine flow rate
- (5) Diluted brine flow rate

12.3.2 Bi-weekly QA/QC Verifications

In-line flow meters and/or rotameters: clean equipment to remove any debris or biological buildup and verify flow volumetrically to avoid erroneous readings.

12.3.3 QA/QC Verifications for Each Test Period

- (1) In-line conductivity meters
- (2) Differential pressure transmitters (verify gauge readings and electrical signal using a pressure meter)
- (3) Tubing (verify good condition of all tubing and connections, replace if necessary)

12.4 On-Site Analytical Methods

The analytical methods utilized in this study for on-site monitoring of raw water and treated water quality are described in the section below. Use of either bench-top or in-line field analytical equipment will be acceptable for the verification testing; however, in-line pH and conductivity meters (located on each column effluent in a fixed-bed plant) are recommended for ease of operation.

12.4.1 pH

- (1) pH analysis shall be performed according to Standard Method 4500-H⁺.
- (2) A 2-point calibration of the pH meter shall be performed once per day when the instrument is in use.
- (3) Certified pH buffers in the expected range shall be used.
- (4) The pH probe shall be stored in the appropriate solution defined in the instrument manual.
- (5) The water is poorly buffered, pH measurement in a confined vessel is recommended to minimize the effects of carbon dioxide exchange with the atmosphere.

12.4.2 Sulfate, Nitrate, Chloride and Alkalinity by Test Kits

Sulfate, nitrate, chloride, and alkalinity (bicarbonate) are not target contaminants for arsenic removal by ion exchange, but they can give indication as to the degree of exhaustion of a column and the approach of arsenic breakthrough. Thus, they may be measured on-site by properly calibrated test kits. Nitrate may be a special case; if the Initial Plant Characterization tests indicate that nitrate will potentially exceed its MCL, nitrate analysis becomes a primary measure of plant performance and nitrate should be determined at a state-certified or third-party or EPA-accredited laboratory, although on-site test kits may also be used to indicate the plant performance.

All test kits used on site should be calibrated daily using known standards at two or more concentration levels. Data obtained with test kits, which utilize non-standard methods shall not be used to determine if the plant meets the applicable performance criteria.

12.4.3 Conductivity

Electrical conductivity (μS or microSiemens) is continuously measured at the outlet of each ion exchange column to indicate when the unit is in exhaustion, regeneration, or rinse mode. Its most important function is to indicate the degree of rinsing of a column following regeneration. If the column is put back into service too soon, arsenic from the spent regenerant salt solution remaining in the column may get into the plant effluent. Thus, it is necessary to check and calibrate the conductivity probes at least once per test period. Conductivity shall be measured using Standard Method 2510 B.

12.4.4 Temperature (Optional for Ion Exchange)

Temperature is not a very important variable in ion exchange providing that the water is less than about 80°C to prevent damage to the strong-base anion resin. If however, the ground water is naturally hot and has been cooled prior to ion exchange treatment and distribution, temperature measurement may be required. Generally, temperature is an optional measurement for the ion exchange process. If required, readings for temperature shall be conducted in accordance with Standard Method 2550. Raw water temperatures should be obtained at least once daily. The thermometer shall have a scale marked for every 0.1°C , as a minimum, and should be calibrated weekly against a precision thermometer certified by the National Institute of Standards and Technology (NIST).

12.4.5 Color

If a surface water is being treated by ion exchange, color measurement may be required. Normally, however, color would be an optional measurement. If it is required, true color shall be measured with a spectrophotometer at 455 nm, using a Hach Company adaptation of the *Standard Methods* 2120 procedure. Samples should be collected in clean plastic or glass bottles and analyzed as soon after collection as possible. If samples can not be analyzed immediately they should be stored at 4°C for up to 24 hours, and then warmed to room temperature before analysis. The filtration system described in *Standard Methods* 2120 C should be used, and results should be expressed in terms of PtCo color units.

12.5 Chemical and Biological Samples Shipped Off-Site for Analyses

Inorganic chemical samples, including arsenic, alkalinity, iron, and manganese, shall be collected and preserved in accordance with Standard Method 3010B, paying particular attention to the sources of contamination as outlined in Standard Method 3010C. The samples should be refrigerated at approximately 2 to 8°C immediately upon collection, shipped in a cooler, and maintained at a temperature of approximately 2 to 8°C . Samples shall be processed for analysis

by a state-certified or third party or EPA-accredited laboratory within 24 hours of collection. The laboratory shall keep the samples at approximately 2 to 8°C until initiation of analysis.

TOC samples shall be collected in glass bottles supplied by the state-certified or third party or EPA-accredited laboratory and shipped at 4 °C to the analytical laboratory as soon as practical. The TOC samples shall be collected and preserved in accordance with Standard Method 5010B.

Algae samples shall be preserved with Lugol's solution after collection, stored and shipped in a cooler at a temperature of approximately 2 to 8°C, and held at that temperature range until counted.

13.0 OPERATIONS & MAINTENANCE (O&M)

The Field Testing Organization shall obtain the Manufacturer-supplied O&M Manual to evaluate the instructions and procedures for their applicability during the verification testing period. The following are recommendations for criteria for O&M Manuals for package plants employing ion exchange.

13.1 Maintenance

The Manufacturer should provide readily understood information on the recommended or required maintenance schedule for each piece of operating equipment such as:

- (1) Ion-exchange beds containing strong-base anion resin
- (2) Multiple parallel fixed beds
- (3) Carousel ion-exchange system, if applicable
- (4) Pumps
- (5) NaCl Brine saturator
- (6) Brine dilutor
- (7) Flow control valves
- (8) Chemical feeders
- (9) Mixers
- (10) Motors
- (11) Instruments, such as continuous pH monitors or conductivity meters
- (12) Integrating Flow meters
- (13) In-line static mixers
- (14) Tanks and basins, especially brine storage tanks

13.2 Operation

13.2.1 Operation Manuals:

The Manufacturer should provide readily understood recommendations for procedures related to proper operation of the package-plant equipment. Among the operating aspects that should be discussed are the following:

Automated Ion Exchange Systems

- (1) Fixed beds
- (2) Multiple fixed beds in parallel, typically three in service and one in standby or regeneration
- (3) Carousels (multiple rotating beds in parallel)

Automated single ion exchange column operation

- (1) Begin exhaustion (service) cycle
- (2) End exhaustion cycle
- (3) Start Backwash
- (4) End Backwash
- (5) Start regeneration
- (6) End regeneration
- (7) Start slow (displacement) rinse
- (8) End slow rinse
- (9) Start fast rinse
- (10) End fast rinse
- (11) Return to service

Chemical feeders (e.g. for NaCl brine preparation and delivery)

- (1) Dilution of brine -- proper procedures
- (2) Calibration check
- (3) Settings and adjustments -- how they should be made

Mixers (if arsenic spiking is employed)

- (1) Purpose
- (2) Changing intensity (RPM), if available

Pressure Filtration (if prefiltration before ion-exchange columns is required)

- (1) Control of filtration rate
- (2) Observation and measurement of head loss during filter run
- (3) Automatic backwashing

13.2.2 Troubleshooting Guide:

The Manufacturer should provide a troubleshooting guide; a simple check-list of what to do for a variety of problems including:

- (1) No raw water (feed water) flow to plant
- (2) Carousel will not turn
- (3) Master carousel valve not functioning
- (4) Ion exchange column effluent pH too low
- (5) No brine flow
- (6) No ion-exchange column backwash flow
- (7) Can't control rate of flow of water through package plant
- (8) No chemical feed (brine, chlorine, or arsenic spiking solution)
- (9) Calibration and maintenance of on-line pH monitoring instruments, problems of erratic pH or drifting pH readings
- (10) No reading on pH meter and/or conductivity meter
- (11) Product water conductivity too high
- (12) No electric power
- (13) Mixer (for arsenic spiking) will not operate
- (14) Pressure prefilter can't be backwashed or backwash rate of flow can't change
- (15) Automatic operation (if provided) not functioning
- (16) No ion-exchange column head loss readings
- (17) Flow control valve stuck or will not operate

13.2.3 History of Ion Exchange Package Plant Operability:

During Verification Testing, attention shall be given to package plant operability aspects. These aspects of plant operation should be included to the extent practical in reports of package plant testing when the testing is done under the NSF Verification Program. Among the factors that should be considered are the following:

- (1) How successful is a SCADA system, i.e., complete automation and computer control with data acquisition as a means of operating an arsenic ion-exchange plant?
- (2) How does one ensure that arsenic has not broken through the column without actually making a continuous on-line arsenic measurement, which is impractical.
- (3) Is there any easy-to-measure parameter such as pH or sulfate concentration that would signal the breakthrough of arsenic from a column?
- (4) How does the operator ensure that the regenerant brine has actually been fed to the spent resin column?
- (5) What is the preferred means of measuring or estimating brine consumption?
- (6) How many times can the brine be reused without treatment
- (7) How does one automate the precipitation of arsenic from the spent brine?
- (8) Does reuse of the brine cause any precipitation problems?
- (9) How often is it necessary to reset the brine flow rate?
- (10) How can plant operator check on condition and depth of ion-exchange media?
- (11) Can ion exchange columns be mothballed in the summer without microbiological growth on the resin?
- (12) What are the special problems encountered in treating surface water using ion exchange for arsenic removal, and it really feasible to use arsenic ion exchange for surface water treatment?

The reports on Verification Testing should address the above questions in the written reports. The issues of operability should be dealt with in the portion of the reports that are written in response to Section 10.3.1 Plant Operating Conditions and Equipment Performance.

14.0 REFERENCES

- Clifford, D. & Lin, C.C. 1991. Arsenic (III) and Arsenic (V) Removal From Drinking Water in San Ysidro, New Mexico, EPA/600/52-91/001. Cincinnati, Ohio (June).
- Clifford, D. A. & C. C. Lin, "Arsenic Removal from Groundwater in Hanford, California—A Preliminary Report," University of Houston, Department of Civil/Environmental Engineering, 1986.
- Clifford, D. A. & Ghurye, G. Ion Exchange With Spent Brine Recycling As A Viable Treatment Technology For Arsenic Removal From Drinking Water, In preparation for submission to J. AWWA, April, 1998.
- Clifford, D.A. & Bilimoria, M. Mobile Drinking Water Treatment Research Facility for Inorganic Removal. EPA-600/S2-84/018 (1978).

- Clifford, D.A. & Lin, C.C. Ion Exchange, Activated Alumina, and Membrane Processes For Arsenic Removal From Groundwater. Proc. 45th Annual Environmental Engineering Conf. Univ. of Kansas (1995).
- Clifford, D.A. 1990. Ion Exchange and Inorganic Adsorption. *Water Supply and Treatment: A Handbook of Community Water Supplies, 4th ed.* McGraw-Hill, New York.
- Cullen, W.R., & Reimer, K. J. 1989. "Arsenic Speciation in the Environment." *Chemistry Review*, 89:713.
- Eaton, A.D. 1994, "Determining the Practical Quantitation Level for Arsenic," *Journal AWWA*, 86:2:100 (February).
- Edwards, Marc, Sapna Patel, Laurie McNeill, Hsiao-wen Chen, Michelle Frey, Andrew Eaton, Ronald C. Antweiler, and Howard E. Taylor. 1998. "Considerations in As Analysis and Speciation," *Journal AWWA*, 90:3:103.
- Ferguson, J. F. & Gavis, J. A., 1972, "A Review of the Arsenic Cycle in Natural Waters." *Water Research*, 6:1259.
- Fox, K.R., & Sorg, T.J. 1987. "Controlling Arsenic, Fluoride, and Uranium by Point-of-Use Treatment," *Journal AWWA*, 79:10:81.
- Frank, P. & D. A. Clifford, *Arsenic(III) Oxidation and Removal from Drinking Water*, PB 86-158 607/ NTIS, Springfield, Va., 1986; *Summary Report*, EPA/600/5286/021, U.S. EPA, Cincinnati, April 1986.
- Frey, M. M., M. A. Edwards, et al. (1997). National Compliance assessment and costs for the regulation of arsenic in drinking water. Denver CO, American Water Works Association.
- Ghurye, G. L., D. A. Clifford, et al. (1998). "Combined Arsenic and Nitrate removal by ion exchange and KDF media." American Water Works Assoc.
- Gulledge, J.H. & O'Connor, J.T. 1973, "Removal of Arsenic From Water by Adsorption on Aluminum and Ferric Hydroxides," *Journal AWWA*, 65:8:548 (August).
- Gupta, S.K. & Chen, K.Y. 1978, "Removal of Arsenic From Water by Adsorption on Aluminum and Ferric Hydroxides," *Journal WPCF*, 50:493 (March).
- Guter, G. (1998). IX Windows Pro. Bakersfield, California, Cathedral Peak Software.
- Hach Water Analysis Handbook*, 2nd Ed. Hach Company, Loveland, Colorado 1992.
- Hathaway, S. and F. Rubel Jr. (1987). "Removing arsenic from drinking water." American Water Works Association Journal 79 (No. 8): 61-65.

Horng, L. L. and D. A. Clifford (1997). "The behavior of polyprotic anions in ion exchange resins." Reactive and Functional Polymers 35 (1/2): 41-54.

Irgolic, K. J., *Speciation of Arsenic Compounds in Water Supplies*, EPA 600/S1-82010, Cincinnati, Ohio, November 1982.

Malcolm Pirnie, Inc. 1993. Treatment and Occurrence, Arsenic in Potable Water Supplies. Drinking Water Treatment Branch, Office of Groundwater and Drinking Water, US Environmental Protection Agency, Washington, D.C., September.

Pontius, F. W. (1995). "An update of the federal drinking water regulations." Journal of the American Water Works Association 87 (2): 48-58.

Smith, A.H. et al. Cancer Risks From Arsenic In Drinking Water. *Environmental Health Perspective*, 97:259 (1992).

Sorg, T. J., & Logsdon, G. S. 1978. "Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 2," *Journal AWWA*, 70:7:379.

Standard Methods for the Examination of Water and Wastewater, 1992. APHA, AWWA, and WPCF, 18th ed., Washington, D.C.

Thompson, M.A., And Chowdhury, Z.K. 1993. Evaluating Arsenic Removal Technologies. Proceedings 1993 AWWA Annual Conference, Water Resources. AWWA, Denver, Colorado, pp. 321-342.

Tirupanangadu, M. (1996). A visual basic application for multicomponent chromatography in ion exchange columns. Environmental Engineering Program. Houston, University of Houston: 179.